# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-263049
(43)Date of publication of application : 07.10.1997

(51)Int.Cl. B41M 5/26

(21)Application number : 08-072226
(22)Date of filing : 27.03.1996

(71)Applicant : RICOH CO LTD
(72)Inventor : MORI YASUTOMO
MORITA MITSUNOBU
NARUSE MITSURU
KAJIKAWA TAKESHI

## (54) THERMOSENSITIVE RECORDING MATERIAL

(57)Abstract:
PROBLEM TO BE SOLVED: To improve resistance against a plasticizer, heat resistance and water resisting property by using a core-shell emulsion in the presence of an acrylic polymer or an acrylic copolymer seed emulsion, as resin and a carbodiimide as a crosslinking agent, in a recording material consisting of a protecting layer formed on a thermosensitive recording layer.
SOLUTION: In a thermosensitive recording material consisting of a protecting layer containing resin and a crosslinking agent formed on a thermosensitive recording layer, a core-shell emulsion obtained by polymerizing acrylamide and/or methacrylamide in the presence of an acrylic polymer or an acrylic copolymer seed emulsion is used as resin, while a carbodiimide compound is used as a crosslinking agent. In addition, this resin has a glass transition point Tg of at least 15° C for the core part and a glass transition point Tg of at least 150° C for the shell part. Further, pigment is used and the pigment/resin ratio is 1 or less. Besides, the oil absorption amount of the pigment is 250cc/100g or less and the average grain diameter thereof is 3μm or less.

LEGAL STATUS

| | |
|---|---|
| [Date of request for examination] | 12.07.2001 |
| [Date of sending the examiner's decision of rejection] | |
| [Kind of final disposal of application other than the examiner's decision of rejection or application converted registration] | |
| [Date of final disposal for application] | |
| [Patent number] | 3563867 |
| [Date of registration] | 11.06.2004 |
| [Number of appeal against examiner's decision of rejection] | |
| [Date of requesting appeal against examiner's decision of rejection] | |
| [Date of extinction of right] | |

---

CLAIMS

---

[Claim(s)]
[Claim 1] The thermal recording ingredient characterized by being the core shell mold emulsion from which this resin carries out the polymerization of acrylamide and/or the methacrylamide, and is obtained under existence of the seed emulsion of an acrylic polymer or a copolymer in the thermal recording ingredient which prepared the heat-sensitive recording layer which carries out coloration with heat on the base material, and prepared the protective layer containing resin and a cross linking agent on this heat-sensitive recording layer further, and this cross linking agent being a carbodiimide compound.
[Claim 2] The thermal recording ingredient according to claim 1 characterized by the glass transition point Tg of the core section of this resin being 15 degrees C or more.
[Claim 3] The thermal recording ingredient according to claim 1 characterized by the glass transition point Tg of the shell section of this resin being 150 degrees C or more.
[Claim 4] The thermal recording ingredient according to claim 1 with which the glass transition point Tg of the core section of this resin is characterized by the glass transition point Tg of 15 degrees C or more and the shell section being 150 degrees C or more.
[Claim 5] Furthermore, claim 1 which uses a pigment together and is characterized by a pigment / resin ratio being one or less thru/or a thermal recording ingredient given in four.
[Claim 6] The thermal recording ingredient according to claim 5 with which oil absorption of this pigment is characterized by 250 cc / 100g or less, and the mean particle diameter of those being 3 micrometers or less.

---

[Translation done.]

## DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the flame radiation angle degree adjustable structure of the burner tile used for a glass tank furnace.
[0002]
[Description of the Prior Art] Conventionally, the burner installed in a glass melting furnace is used in various locations, such as a founding tub and a melting basin. What is used for the founding tub by which hand gathering is performed to below as the example is shown.
[0003] The founding tub used for hand gathering is having structure as shown in drawing 4 , and the glass kind winding rod entrance 101, the overflow opening 102, and the opening 103 for burner installation are formed in the furnace wall of a founding tub. The glass kind winding rod entrance 101 is formed in the side attachment wall of the right opposite of the side attachment wall joined to the throat 104, the overflow opening 102 is formed in the side attachment wall contiguous to this side attachment wall, and the opening 103 for burner installation is formed in the side attachment wall contiguous to the side attachment wall which is the opposite side of a side attachment wall in which this overflow opening 102 was formed, and is joined to the throat 104.
[0004] The glass component volatilized, and the overflow opening 102 was formed in order to carry out outflow removal of the bubble produced by the melting glass drop which falls from a glass kind winding rod, when taking out the melting glass of the front face made heterogeneous, and a glass kind winding rod out of melting glass. Moreover, the burner 105 for adjusting the temperature in a founding tub was inserted and fixed to the furnace wall side and the perpendicular from the furnace wall by the opening 103 for burner installation, and the melting glass near [ in which the throat 106 is formed ] the furnace wall was heated to it.
[0005]
[Problem(s) to be Solved by the Invention] However, in a founding tub which was described above, since it is heating with the flame of the burner which had melting glass near [ in which the throat is formed ] the furnace wall fixed, the convection current of melting glass is small. Consequently, since the bubble produced by the melting glass drop also flowed in accordance with this convection current, when the bubble generated on the front face was not able to be completely poured to overflow opening, but a glass kind winding rod was put in into melting glass and a glass kind was rolled round, a bubble mixes into a glass kind and it was easy to make glass mold goods generate a poor bubble.
[0006] Moreover, if the burner used not only for the burner used for this founding tub but for a glass melting furnace fixes the location and direction of a burner at the time of the furnace construction of a glass melting furnace, or ****, the location and direction of a burner are fixed till the next furnace construction or ****. For this reason, also in the burner used for a melting basin, since the flame is emitted to the fixed location, when the non-melting raw material which is floating in a melting basin cannot be fused completely, the defect from whom a non-melting raw material mixes in the melting glass for shaping, and a non-melting raw material becomes a cause at glass mold goods will arise.
[0007] Therefore, this invention aims at losing the bubble on the non-melting raw material on the melting glass of the melting basin leading to the defect of glass mold goods, or the melting glass of a founding tub using the flame of a burner.
[0008]
[Means for Solving the Problem] In order that this invention might solve a technical problem, invention corresponding to claim 1 surrounded a part of said curved surface of the burner tile with which the curved surface was formed in the outside surface inserted in the hole of opening prepared in the furnace wall of a glass melting furnace, and the hole of this opening, and this burner tile, consisted of a hole of said opening, and a burner block which fits in, and was equipped with the flame radiation angle degree adjustable structure which enabled tilting of the flame irradiation hole of this burner tile in the direction of arbitration. Thus, it can be made hard to be able to make the tilt of the flame irradiation hole of a burner tile carry out in the direction of arbitration, separating the inside of a furnace, and the outside of a furnace by surrounding a part of curved surface of a burner tile with a burner block, and to escape the heat in a furnace out of a furnace. So, when this invention is applied to a melting basin, a flame can be emitted aiming at the non-melting raw material which exists on melting glass, and a non-melting raw material can be fused. Moreover, when it applies to a founding tub, a flame is emitted aiming at the bubble produced on melting glass, it can expand a bubble and eliminate or surface flow of melting glass can be expanded for the convection current of the melting glass which contains the bubble of a melting glass front face by change of temperature distribution as a big thing.
[0009] It was made for invention corresponding to claim 2 to make an unguent placed between the clearances produced between a burner block and a burner tile. By carrying out like this, a burner tile can be moved easily.
[0010] Invention corresponding to claim 3 formed the taper so that the inside side of a furnace wall might be extended to a burner block. By carrying out like this, even if it makes the tilt of the flame irradiation hole carry out in the direction of arbitration, the flame emitted to a burner block from a flame irradiation hole stops being able to interfere easily.
[0011] It is made for invention corresponding to claim 4 to spray Ayr towards the inside of a furnace from the furnace outside of the hole of opening with which a burner tile is inserted. By carrying out like this, it can prevent that Ayr passes between a burner tile and a burner block, and the vapor generated in a glass melting furnace invades and adheres.
[0012] Invention corresponding to claim 5 consisted of burner tiles of the shape of the shape of a truncated cone by which the diameter of the point inserted in the hole of opening prepared in the furnace wall of a glass melting furnace and the hole of this opening was reduced rather than the back end section, and a truncated pyramid, and enabled tilting of the flame irradiation hole of

said burner tile in the direction of arbitration. By having done in this way, the flame irradiation hole of a burner tile can be tilted in the direction of arbitration, with the inside of a furnace, and the outside of a furnace separated. So, when this invention is applied to a melting basin, a flame can be emitted aiming at the non-melting raw material which exists on melting glass, and a non-melting raw material can be fused. Moreover, when it applies to a founding tub, a flame is emitted aiming at the bubble produced on melting glass, it can expand a bubble and eliminate or surface flow of melting glass can be expanded for the convection current of the melting glass which contains the bubble of a melting glass front face by change of temperature distribution as a big thing.
[0013] Invention corresponding to claim 6 formed the taper so that the inside side of a furnace wall might be extended to the hole of opening indicated by invention corresponding to claim 5. Even if it tilts the flame radiation direction of a burner tile in the direction of arbitration by having considered as such structure, the flame emitted from a burner tile stops being able to interfere with a furnace wall easily.
[0014]
[Embodiment of the Invention] The gestalt of operation of this invention is explained with reference to drawing 1 thru/or drawing 3 .

[0015] (Gestalt 1 of operation) The gestalt 1 of this operation uses the flame radiation angle degree adjustable structure of the burner tile of this invention for the furnace wall of the founding tub of a glass melting furnace which performs hand gathering. Adjustable structure is notionally shown in drawing 1 whenever [ flame radiation angle / of this burner tile ]. In order to separate the inside of a founding tub, and the outside of a furnace with the gestalt 1 of this operation and to make whenever [ flame radiation angle ] adjustable The burner tile 1 which determines whenever [ flame radiation angle ], and the burner 2 joined to the back end of this burner tile 1, The burner block 3 which surrounds a part of globular form section of a burner tile 1, the hole 5 of opening of the furnace wall 4 in which this burner block 3 is inserted, and the Ayr pipe 6 which sprays Ayr between a burner tile 1 and the burner block 3 from the furnace outside of a furnace wall 4 are provided. In addition, it is fixed to the fixed facility which is not illustrated and the burner 2 is having the location held.
[0016] The burner tile 1 is also really casting the hardware 7 attached in the point of a burner 2, when casting. And the burner tile 1 and the burner 2 are used as one by joining the hardware 7 and the burner 2 of a burner tile 1. As for the configuration of this burner tile 1, the globular form is carried out near the flame irradiation hole like the bulb for electric bulbs in an appearance.
[0017] The burner block 3 is formed by outer block 3b formed in inner-block 3a and the furnace outside which were formed in the furnace inside so that the globular form section of a burner tile 1 might be inserted on the furnace inside and the furnace outside of a hole 5 of opening. And inner-block 3a has wrapped in a part of globular form section of a burner tile 1 so that the flame irradiation hole of a burner tile 1 may not be made to project in a furnace from inner-block 3a. By carrying out like this, the flame irradiation hole of a burner tile 1 stops being influenced of the radiant heat in a furnace easily, and can lengthen the life of a burner tile 1.
[0018] Moreover, when a burner tile 1 is moved in the direction of arbitration, such as four directions, and the flame radiation direction is made to change, from the flame irradiation hole of a burner tile 1, inner-block 3a is the furnace inside, and has the taper extended by the furnace inside so that a flame may not interfere with inner-block 3a. When moving a burner tile 1 in the direction of arbitration, such as four directions, outer block 3b has the taper with which a furnace outside extends outer block 3b into the part which does not wrap in the globular form section of a burner tile 1 like inner-block 3a so that it may be convenient.
[0019] The Ayr pipe 6 passes along the clearance which Ayr produces from the outside of a furnace between a burner tile 1 and the burner block 3, and it has installed it outside the furnace so that it may blow in into a furnace. This Ayr is for making it for volatile matter, dust, etc. of glass which are called the vapor adhering to a furnace wall to the clearance produced between a burner tile 1 and the burner block 3 to invade, and not adhere. So, this Ayr is blowing off at a rate 10m3 / beyond time amount continuously during operation of a glass melting furnace, and that pressure is more than 10mH(s)2 O.
[0020] A change of whenever [ flame radiation angle / of the burner tile 1 shown above ] is made by moving the burner connected to this burner tile 1.
[0021] By having shown adjustable structure above whenever [ flame radiation angle / of a burner tile 1 ], vapor trespasses upon the clearance produced between a burner tile 1 and the burner block 3, and it does not adhere, but a burner tile 1 can be moved in the direction of arbitration, such as four directions. Therefore, by turning the flame of a burner 2 near the melting glass side a glass kind winding rod is taken in and out of which, it can expand the bubble produced in the melting glass drop dropped from a glass kind winding rod and eliminate, or the surface flow of melting glass can be expanded for the convection current of melting glass as a big thing, and a bubble can be poured to overflow opening. Therefore, since it can avoid rolling round the melting glass containing the bubble on the front face generated at the time of hand gathering pointed out with the above-mentioned technical problem with a glass kind winding rod, a defect with a bubble stops being able to generate it easily in glass mold goods from the melting glass rolled round with the glass kind winding rod.
[0022] In addition, although a point like an electric bulb bulb used the configuration of a burner tile 1 as the object which is carrying out the globular form with the gestalt 1 of the above operation, if the part surrounded with the burner block 3 of a burner tile 1 has curved surfaces, such as a globular form or a cylindrical shape, without being limited to this, the tilt of a burner tile 1 will become possible within the burner block 3. Here, as for the cylindrical burner tile 1, the part by which the part surrounded with the burner block 3 is joined to a burner 2 is presenting the appearance of a T character mold by forming a flame irradiation hole in a projection and the curved surface of the opposite side of this lobe from a cylindrical curved surface. Since the burner tile 1 of this cylindrical shape can carry out tilt of the burner tile 1 along with a cylindrical arc, when carrying out tilt of the burner tile 1 only to 2-ways, such as the upper and lower sides or right and left, it is suitable. Moreover, a ceramic ball may be made to be placed between the clearances produced between a burner tile 1 and the burner block 3 as an unguent for performing tilt of a burner tile 1 smoothly.
[0023] (Gestalt 2 of operation) The gestalt 2 of this operation is the modification of adjustable structure whenever [ flame radiation angle / of the burner tile of the gestalt 1 of operation ], and is notionally shown in drawing 2 . The gestalt 2 of this operation consists of a burner tile 1 which determines whenever [ flame radiation angle / which is inserted in the hole 5 of opening with which the taper was formed in the furnace wall inside side of the furnace wall of a founding tub, and the hole 5 of this opening ], and a burner 2 connected to the back end of this burner tile 1. In addition, it is fixed to the fixed facility which is not illustrated and the burner 2 is having the location held.
[0024] Like [ the gestalt 2 of this operation ] the gestalt 1 of the above-mentioned implementation, the burner tile 1 is also really casting the hardware 7 attached in the point of a burner 2, when casting. And the burner tile 1 and the burner 2 are used as one by joining the hardware 7 and the burner 2 of a burner tile 1. In addition, it provides the taper so that the configuration of a burner tile 1 is close to a flame irradiation hole, and it may become a taper, and it may become the shape of the shape of a truncated cone, and a truncated pyramid.

[0025] The same configuration as a cutting plane perpendicular to the path of insertion of a burner tile 1 is carried out, the taper which has a furnace wall side extended is formed so that it may not interfere in a furnace wall side with the flame of a burner 2, and the hole 5 of opening formed in the furnace wall has a diameter of opening smaller than the part of the overall diameter of a burner tile 1. When a burner tile 1 is inserted in the hole 5 of opening, it inserts until a burner tile 1 and the hole 5 of opening contact. Moreover, like the gestalt 1 of the above-mentioned implementation, the flame irradiation hole of a burner tile 1 is inserted so that it may not project from a furnace internal surface. The taper formed in the taper and the furnace wall inside which were formed in the burner tile 1 can determine the tilt range of a burner tile 1.
[0026] A change of whenever [ flame radiation angle / of the burner tile 1 shown above ] is made by moving the burner 2 connected to the burner tile 1 like the gestalt 1 of the above-mentioned implementation. Moreover, since the burner tile 1 is not being fixed to the furnace wall, when inserting a burner tile 1 in the hole 5 of opening, after connecting a burner tile 1 to a burner 2, it is made to carry out in the case of the gestalt 2 of this operation.
[0027] By having made adjustable structure above whenever [ flame radiation angle / of a burner tile 1 ], the insertion angle into the furnace of a burner tile 1 can be changed easily, without missing the heat in a furnace out of a furnace. For this reason, by turning the flame radiation direction of a burner 2 near the melting glass side a glass kind winding rod is taken in and out of which, it can expand the bubble produced in the melting glass drop dropped from a glass kind winding rod and eliminate, or the surface flow of melting glass can be expanded for the convection current of melting glass as a big thing, and a bubble can be poured to overflow opening. Therefore, since it can avoid rolling round the melting glass containing the bubble on the front face generated at the time of hand gathering pointed out with the above-mentioned technical problem with a glass kind winding rod, a defect with a bubble stops being able to generate it easily in glass mold goods from the melting glass rolled round with the glass kind winding rod.
[0028] It inserts until a burner tile 1 contacts the hole 5 of opening, when inserting a burner tile 1 in the hole 5 of opening, but [ the gestalt 2 of the above operation ] or it inserts a burner tile 1 in the hole 5 of opening in the state of non-contact, the path of the hole 5 of opening may be made larger than the overall diameter of a burner tile 1, and a burner tile 1 may be inserted in the hole 5 of opening. Since a clearance is generated between the hole 5 of opening, and a burner tile 1 in these cases, the heat in a furnace is made not to escape this clearance out of a furnace using sealants, such as mortar or a blanket. And after once removing a sealant and fixing an include angle, it is made for a sealant to close a clearance again, when changing the include angle of a burner tile 1.
[0029] The example of adjustable structure can be used also for the burner 2 of a melting basin whenever [ flame radiation angle / which was shown with the gestalten 1 and 2 of the above operation ]. When it uses for the burner 2 of a melting basin, effectiveness as taken below is done so.
[0030] 1. When the batch crest of the raw materials for glass which are floating in a melting basin has reached to near the front wall of a melting basin, or when it has floated near a detached building front wall from the batch crest of raw materials for glass with non-melting, the flame of a burner can be emitted aiming at the tip of a batch crest, or a suspension non-melting raw material. So, the poor glass from which the tip of a batch crest is pulled back to a doghouse side, or it becomes possible from which to fuse completely the non-melting raw material which separates from a batch crest and is floating in a melting basin, and a non-melting raw material becomes a cause at glass mold goods can be reduced.
[0031] 2. When the location at the tip of a batch crest gets mixed up by change of the input of raw materials for glass etc. in the case of the glass melting furnace to which the flame of the tip ****** burner 2 of a batch crest is emitted from the side attachment wall by the side of a front wall from the point of the batch crest of the raw materials for glass which are floating in a melting basin, whenever [ flame radiation angle / of a burner 2 ] can be changed, and it can follow in footsteps at the tip of a batch crest.
[0032] 3. When the hot spots in the melting basin at the time of a glass melting furnace design differ rather than the location which was being planned at the beginning, the location which changes whenever [ flame radiation angle / of a burner 2 ], corrects the hot spot in a melting basin, and is considered as a request can be made to produce a hot spot.
[0033] (Gestalt 3 of operation) the gestalt 3 of this operation is the burner 2 used for the furnace wall of the melting basin of a glass melting furnace, whenever [ flame radiation angle / of the gestalt 1 of the above-mentioned implementation ], in adjustable structure, is an example when using at which secondary air is used, and is notionally shown in drawing 3 . The gestalt 3 of this operation connects the burner casing 8 to the back end of a burner tile 1 in the flame radiation angle degree adjustable structure shown with the gestalt 1 of the above-mentioned implementation.
[0034] This burner casing 8 has the burner-tile end connection 9 connected with a burner tile 1, the burner insertion opening 10 with which a burner 2 is inserted, and the secondary air induction inlet 11 which introduces secondary air.
[0035] When leaning whenever [ flame radiation angle / of the burner 2 using this burner casing 8 ] in the direction of arbitration, a burner tile 1, the burner casing 8, and a burner 2 move together. At the time of this tilt actuation, the burner 2 is fixed to the burner casing 8 so that the pin center,large of the burner 2 inserted in the burner casing 8 may not shift.
[0036] Thus, since the heating value of the flame of a burner 2 other than the effectiveness explained above by adopting adjustable structure as the burner 2 using the secondary air used for the melting basin of a glass melting furnace whenever [ flame radiation angle / of this invention ] increases, adjustable structure is [ whenever / flame radiation angle / of this invention ] employable also as the furnace where the melting capacity of a glass melting furnace is big.
[0037] In addition, with the gestalt 3 of this operation, although the flame radiation angle degree adjustable structure of the gestalt 1 of operation was used, the flame radiation angle degree adjustable structure of the gestalt 2 of operation may be used.
[0038]
[Effect of the Invention] It can be made hard for invention corresponding to claim 1 to be able to make the tilt of the flame irradiation hole of a burner tile carry out in the direction of arbitration, separating the inside of a furnace, and the outside of a furnace by surrounding a part of curved surface of a burner tile with a burner block, and to escape the heat in a furnace out of a furnace. For this reason, the flame radiation direction of a burner can be easily changed also in operation of a glass melting furnace. So, when this invention is applied to a melting basin, a flame can be emitted aiming at the non-melting raw material which exists on melting glass, and a non-melting raw material can be fused. Moreover, when it applies to a founding tub, a flame is emitted aiming at the bubble produced on melting glass, it can expand a bubble and eliminate or a bubble can be moved. Therefore, a non-melting raw material, a bubble, etc. stop easily being mixed with the melting glass used for glass shaping.
[0039] Invention corresponding to claim 2 can move a burner tile easily by having made it make an unguent placed between the clearances produced between a burner tile and a burner block.
[0040] Invention corresponding to claim 3 is emitted by having formed the taper in the furnace wall inside side of a burner block,

without a burner block interfering in a flame, even if it makes the tilt of the flame irradiation hole carry out in the direction of arbitration. Therefore, a flame can be emitted to the location considered as a request.

[0041] By having made it spray Ayr towards the inside of a furnace from the furnace outside of the hole of opening with which a burner tile is inserted, Ayr passes between a burner tile and a burner block, and invention corresponding to claim 4 can prevent the vapor generated in a melting furnace between a burner tile and a burner block invading and adhering, and even if the busy period of a melting furnace continues at a long period of time, it can tilt the flame irradiation hole of a burner tile in the direction of arbitration easily.

[0042] Invention corresponding to claim 5 makes a furnace wall inside side taper structure at the hole of opening prepared in the furnace wall of a glass melting furnace. By having made the burner tile inserted in the hole of this opening into the shape of a truncated cone and truncated-pyramid-like structure where the diameter of a point was reduced rather than the back end section It can be made hard to be able to tilt the flame irradiation hole of a burner tile in the direction of arbitration, with the inside of a furnace, and the outside of a furnace separated, and to escape the heat in a furnace out of a furnace. For this reason, the flame radiation direction of a burner can be easily changed also in operation of a glass melting furnace. So, when this invention is applied to a melting basin, a flame can be emitted aiming at the non-melting raw material which exists on melting glass, and a non-melting raw material can be fused. Moreover, when it applies to a founding tub, a flame is emitted aiming at the bubble produced on melting glass, it can expand a bubble and eliminate or a bubble can be moved. Therefore, a non-melting raw material, a bubble, etc. stop easily being mixed with the melting glass used for glass shaping.

---

[Translation done.]

## TECHNICAL FIELD

[Field of the Invention] This invention relates to the flame radiation angle degree adjustable structure of the burner tile used for a glass tank furnace.

[Translation done.]

---

PRIOR ART

---

[Description of the Prior Art] Conventionally, the burner installed in a glass melting furnace is used in various locations, such as a founding tub and a melting basin. What is used for the founding tub by which hand gathering is performed to below as the example is shown.

[0003] The founding tub used for hand gathering is having structure as shown in drawing 4 , and the glass kind winding rod entrance 101, the overflow opening 102, and the opening 103 for burner installation are formed in the furnace wall of a founding tub. The glass kind winding rod entrance 101 is formed in the side attachment wall of the right opposite of the side attachment wall joined to the throat 104, the overflow opening 102 is formed in the side attachment wall contiguous to this side attachment wall, and the opening 103 for burner installation is formed in the side attachment wall contiguous to the side attachment wall which is the opposite side of a side attachment wall in which this overflow opening 102 was formed, and is joined to the throat 104.

[0004] The glass component volatilized, and the overflow opening 102 was formed in order to carry out outflow removal of the bubble produced by the melting glass drop which falls from a glass kind winding rod, when taking out the melting glass of the front face made heterogeneous, and a glass kind winding rod out of melting glass. Moreover, the burner 105 for adjusting the temperature in a founding tub was inserted and fixed to the furnace wall side and the perpendicular from the furnace wall by the opening 103 for burner installation, and the melting glass near [ in which the throat 106 is formed ] the furnace wall was heated to it.

---

[Translation done.]

## EFFECT OF THE INVENTION

[Effect of the Invention] It can be made hard for invention corresponding to claim 1 to be able to make the tilt of the flame irradiation hole of a burner tile carry out in the direction of arbitration, separating the inside of a furnace, and the outside of a furnace by surrounding a part of curved surface of a burner tile with a burner block, and to escape the heat in a furnace out of a furnace. For this reason, the flame radiation direction of a burner can be easily changed also in operation of a glass melting furnace. So, when this invention is applied to a melting basin, a flame can be emitted aiming at the non-melting raw material which exists on melting glass, and a non-melting raw material can be fused. Moreover, when it applies to a founding tub, a flame is emitted aiming at the bubble produced on melting glass, it can expand a bubble and eliminate or a bubble can be moved. Therefore, a non-melting raw material, a bubble, etc. stop easily being mixed with the melting glass used for glass shaping.
[0039] Invention corresponding to claim 2 can move a burner tile easily by having made it make an unguent placed between the clearances produced between a burner tile and a burner block.
[0040] Invention corresponding to claim 3 is emitted by having formed the taper in the furnace wall inside side of a burner block, without a burner block interfering in a flame, even if it makes the tilt of the flame irradiation hole carry out in the direction of arbitration. Therefore, a flame can be emitted to the location considered as a request.
[0041] By having made it spray Ayr towards the inside of a furnace from the furnace outside of the hole of opening with which a burner tile is inserted, Ayr passes between a burner tile and a burner block, and invention corresponding to claim 4 can prevent the vapor generated in a melting furnace between a burner tile and a burner block invading and adhering, and even if the busy period of a melting furnace continues at a long period of time, it can tilt the flame irradiation hole of a burner tile in the direction of arbitration easily.
[0042] Invention corresponding to claim 5 is having made the furnace wall inside side into taper structure at the hole of opening prepared in the furnace wall of a glass melting furnace, and having made the burner tile inserted in the hole of this opening into the shape of a truncated cone and truncated-pyramid-like structure the diameter of a point having been reduced rather than the back end section. It can be made hard to be able to tilt the flame irradiation hole of a burner tile in the direction of arbitration, with the inside of a furnace, and the outside of a furnace separated, and to escape the heat in a furnace out of a furnace. For this reason, the flame radiation direction of a burner can be easily changed also in operation of a glass melting furnace. So, when this invention is applied to a melting basin, a flame can be emitted aiming at the non-melting raw material which exists on melting glass, and a non-melting raw material can be fused. Moreover, when it applies to a founding tub, a flame is emitted aiming at the bubble produced on melting glass, it can expand a bubble and eliminate or a bubble can be moved. Therefore, a non-melting raw material, a bubble, etc. stop easily being mixed with the melting glass used for glass shaping.

[Translation done.]

## TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, in a founding tub which was described above, since it is heating with the flame of the burner which had melting glass near [ in which the throat is formed ] the furnace wall fixed, the convection current of melting glass is small. Consequently, since the bubble produced by the melting glass drop also flowed in accordance with this convection current, when the bubble generated on the front face was not able to be completely poured to overflow opening, but a glass kind winding rod was put in into melting glass and a glass kind was rolled round, a bubble mixes into a glass kind and it was easy to make glass mold goods generate a poor bubble.

[0006] Moreover, if the burner used not only for the burner used for this founding tub but for a glass melting furnace fixes the location and direction of a burner at the time of the furnace construction of a glass melting furnace, or ****, the location and direction of a burner are fixed till the next furnace construction or ****. For this reason, also in the burner used for a melting basin, since the flame is emitted to the fixed location, when the non-melting raw material which is floating in a melting basin cannot be fused completely, the defect from whom a non-melting raw material mixes in the melting glass for shaping, and a non-melting raw material becomes a cause at glass mold goods will arise.

[0007] Therefore, this invention aims at losing the bubble on the non-melting raw material on the melting glass of the melting basin leading to the defect of glass mold goods, or the melting glass of a founding tub using the flame of a burner.

[Translation done.]

MEANS

[Means for Solving the Problem] In order that this invention might solve a technical problem, invention corresponding to claim 1 surrounded a part of said curved surface of the burner tile with which the curved surface was formed in the outside surface inserted in the hole of opening prepared in the furnace wall of a glass melting furnace, and the hole of this opening, and this burner tile, consisted of a hole of said opening, and a burner block which fits in, and was equipped with the flame radiation angle degree adjustable structure which enabled tilting of the flame irradiation hole of this burner tile in the direction of arbitration. Thus, it can be made hard to be able to make the tilt of the flame irradiation hole of a burner tile carry out in the direction of arbitration, separating the inside of a furnace, and the outside of a furnace by surrounding a part of curved surface of a burner tile with a burner block, and to escape the heat in a furnace out of a furnace. So, when this invention is applied to a melting basin, a flame can be emitted aiming at the non-melting raw material which exists on melting glass, and a non-melting raw material can be fused. Moreover, when it applies to a founding tub, a flame is emitted aiming at the bubble produced on melting glass, it can expand a bubble and eliminate or surface flow of melting glass can be expanded for the convection current of the melting glass which contains the bubble of a melting glass front face by change of temperature distribution as a big thing.
[0009] It was made for invention corresponding to claim 2 to make an unguent placed between the clearances produced between a burner block and a burner tile. By carrying out like this, a burner tile can be moved easily.
[0010] Invention corresponding to claim 3 formed the taper so that the inside side of a furnace wall might be extended to a burner block. By carrying out like this, even if it makes the tilt of the flame irradiation hole carry out in the direction of arbitration, the flame emitted to a burner block from a flame irradiation hole stops being able to interfere easily.
[0011] It is made for invention corresponding to claim 4 to spray Ayr towards the inside of a furnace from the furnace outside of the hole of opening with which a burner tile is inserted. By carrying out like this, it can prevent that Ayr passes between a burner tile and a burner block, and the vapor generated in a glass melting furnace invades and adheres.
[0012] Invention corresponding to claim 5 consisted of burner tiles of the shape of the shape of a truncated cone by which the diameter of the point inserted in the hole of opening prepared in the furnace wall of a glass melting furnace and the hole of this opening was reduced rather than the back end section, and a truncated pyramid, and enabled tilting of the flame irradiation hole of said burner tile in the direction of arbitration. By having done in this way, the flame irradiation hole of a burner tile can be tilted in the direction of arbitration, with the inside of a furnace, and the outside of a furnace separated. So, when this invention is applied to a melting basin, a flame can be emitted aiming at the non-melting raw material which exists on melting glass, and a non-melting raw material can be fused. Moreover, when it applies to a founding tub, a flame is emitted aiming at the bubble produced on melting glass, it can expand a bubble and eliminate or surface flow of melting glass can be expanded for the convection current of the melting glass which contains the bubble of a melting glass front face by change of temperature distribution as a big thing.
[0013] Invention corresponding to claim 6 formed the taper so that the inside side of a furnace wall might be extended to the hole of opening indicated by invention corresponding to claim 5. Even if it tilts the flame radiation direction of a burner tile in the direction of arbitration by having considered as such structure, the flame emitted from a burner tile stops being able to interfere with a furnace wall easily.
[0014]
[Embodiment of the Invention] The gestalt of operation of this invention is explained with reference to drawing 1 thru/or drawing 3 .

[0015] (Gestalt 1 of operation) The gestalt 1 of this operation uses the flame radiation angle degree adjustable structure of the burner tile of this invention for the furnace wall of the founding tub of a glass melting furnace which performs hand gathering. Adjustable structure is notionally shown in drawing 1 whenever [ flame radiation angle / of this burner tile ]. In order to separate the inside of a founding tub, and the outside of a furnace with the gestalt 1 of this operation and to make whenever [ flame radiation angle ] adjustable The burner tile 1 which determines whenever [ flame radiation angle ], and the burner 2 joined to the back end of this burner tile 1, The burner block 3 which surrounds a part of globular form section of a burner tile 1, the hole 5 of opening of the furnace wall 4 in which this burner block 3 is inserted, and the Ayr pipe 6 which sprays Ayr between a burner tile 1 and the burner block 3 from the furnace outside of a furnace wall 4 are provided. In addition, it is fixed to the fixed facility which is not illustrated and the burner 2 is having the location held.
[0016] The burner tile 1 is also really casting the hardware 7 attached in the point of a burner 2, when casting. And the burner tile 1 and the burner 2 are used as one by joining the hardware 7 and the burner 2 of a burner tile 1. As for the configuration of this burner tile 1, the globular form is carried out near the flame irradiation hole like the bulb for electric bulbs in an appearance.
[0017] The burner block 3 is formed by outer block 3b formed in inner-block 3a and the furnace outside which were formed in the furnace inside so that the globular form section of a burner tile 1 might be inserted on the furnace inside and the furnace outside of a hole 5 of opening. And inner-block 3a has wrapped in a part of globular form section of a burner tile 1 so that the flame irradiation hole of a burner tile 1 may not be made to project in a furnace from inner-block 3a. By carrying out like this, the flame irradiation hole of a burner tile 1 stops being influenced of the radiant heat in a furnace easily, and can lengthen the life of a burner tile 1.
[0018] Moreover, when a burner tile 1 is moved in the direction of arbitration, such as four directions, and the flame radiation direction is made to change, from the flame irradiation hole of a burner tile 1, inner-block 3a is the furnace inside, and has the taper extended by the furnace inside so that a flame may not interfere with inner-block 3a. When moving a burner tile 1 in the direction of arbitration, such as four directions, outer block 3b has the taper with which a furnace outside extends outer block 3b into the part which does not wrap in the globular form section of a burner tile 1 like inner-block 3a so that it may be convenient.

[0019] The Ayr pipe 6 passes along the clearance which Ayr produces from the outside of a furnace between a burner tile 1 and the burner block 3, and it has installed it outside the furnace so that it may blow in into a furnace. This Ayr is for making it for volatile matter, dust, etc. of glass which are called the vapor adhering to a furnace wall to the clearance produced between a burner tile 1 and the burner block 3 to invade, and not adhere. So, this Ayr is blowing off at a rate 10m3 / beyond time amount continuously during operation of a glass melting furnace, and that pressure is more than 10mH(s)2 O.
[0020] A change of whenever [ flame radiation angle / of the burner tile 1 shown above ] is made by moving the burner connected to this burner tile 1.
[0021] By having shown adjustable structure above whenever [ flame radiation angle / of a burner tile 1 ], vapor trespasses upon the clearance produced between a burner tile 1 and the burner block 3, and it does not adhere, but a burner tile 1 can be moved in the direction of arbitration, such as four directions. Therefore, by turning the flame of a burner 2 near the melting glass side a glass kind winding rod is taken in and out of which, it can expand the bubble produced in the melting glass drop dropped from a glass kind winding rod and eliminate, or the surface flow of melting glass can be expanded for the convection current of melting glass as a big thing, and a bubble can be poured to overflow opening. Therefore, since it can avoid rolling round the melting glass containing the bubble on the front face generated at the time of hand gathering pointed out with the above-mentioned technical problem with a glass kind winding rod, a defect with a bubble stops being able to generate it easily in glass mold goods from the melting glass rolled round with the glass kind winding rod.
[0022] In addition, although a point like an electric bulb bulb used the configuration of a burner tile 1 as the object which is carrying out the globular form with the gestalt 1 of the above operation, if the part surrounded with the burner block 3 of a burner tile 1 has curved surfaces, such as a globular form or a cylindrical shape, without being limited to this, the tilt of a burner tile 1 will become possible within the burner block 3. Here, as for the cylindrical burner tile 1, the part by which the part surrounded with the burner block 3 is joined to a burner 2 is presenting the appearance of a T character mold by forming a flame irradiation hole in a projection and the curved surface of the opposite side of this lobe from a cylindrical curved surface. Since the burner tile 1 of this cylindrical shape can carry out tilt of the burner tile 1 along with a cylindrical arc, when carrying out tilt of the burner tile 1 only to 2-ways, such as the upper and lower sides or right and left, it is suitable. Moreover, a ceramic ball may be made to be placed between the clearances produced between a burner tile 1 and the burner block 3 as an unguent for performing tilt of a burner tile 1 smoothly.
[0023] (Gestalt 2 of operation) The gestalt 2 of this operation is the modification of adjustable structure whenever [ flame radiation angle / of the burner tile of the gestalt 1 of operation ], and is notionally shown in drawing 2 . The gestalt 2 of this operation consists of a burner tile 1 which determines whenever [ flame radiation angle / which is inserted in the hole 5 of opening with which the taper was formed in the furnace wall inside side of the furnace wall of a founding tub, and the hole 5 of this opening ], and a burner 2 connected to the back end of this burner tile 1. In addition, it is fixed to the fixed facility which is not illustrated and the burner 2 is having the location held.
[0024] Like [ the gestalt 2 of this operation ] the gestalt 1 of the above-mentioned implementation, the burner tile 1 is also really casting the hardware 7 attached in the point of a burner 2, when casting. And the burner tile 1 and the burner 2 are used as one by joining the hardware 7 and the burner 2 of a burner tile 1. In addition, it provides the taper so that the configuration of a burner tile 1 is close to a flame irradiation hole, and it may become a taper, and it may become the shape of the shape of a truncated cone, and a truncated pyramid.
[0025] The same configuration as a cutting plane perpendicular to the path of insertion of a burner tile 1 is carried out, the taper which has a furnace wall side extended is formed so that it may not interfere in a furnace wall side with the flame of a burner 2, and the hole 5 of opening formed in the furnace wall has a diameter of opening smaller than the part of the overall diameter of a burner tile 1. When a burner tile 1 is inserted in the hole 5 of opening, it inserts until a burner tile 1 and the hole 5 of opening contact. Moreover, like the gestalt 1 of the above-mentioned implementation, the flame irradiation hole of a burner tile 1 is inserted so that it may not project from a furnace internal surface. The taper formed in the taper and the furnace wall inside which were formed in the burner tile 1 can determine the tilt range of a burner tile 1.
[0026] A change of whenever [ flame radiation angle / of the burner tile 1 shown above ] is made by moving the burner 2 connected to the burner tile 1 like the gestalt 1 of the above-mentioned implementation. Moreover, since the burner tile 1 is not being fixed to the furnace wall, when inserting a burner tile 1 in the hole 5 of opening, after connecting a burner tile 1 to a burner 2, it is made to carry out in the case of the gestalt 2 of this operation.
[0027] By having made adjustable structure above whenever [ flame radiation angle / of a burner tile 1 ], the insertion angle into the furnace of a burner tile 1 can be changed easily, without missing the heat in a furnace out of a furnace. For this reason, by turning the flame radiation direction of a burner 2 near the melting glass side a glass kind winding rod is taken in and out of which, it can expand the bubble produced in the melting glass drop dropped from a glass kind winding rod and eliminate, or the surface flow of melting glass can be expanded for the convection current of melting glass as a big thing, and a bubble can be poured to overflow opening. Therefore, since it can avoid rolling round the melting glass containing the bubble on the front face generated at the time of hand gathering pointed out with the above-mentioned technical problem with a glass kind winding rod, a defect with a bubble stops being able to generate it easily in glass mold goods from the melting glass rolled round with the glass kind winding rod.
[0028] It inserts until a burner tile 1 contacts the hole 5 of opening, when inserting a burner tile 1 in the hole 5 of opening, but [ the gestalt 2 of the above operation ] or it inserts a burner tile 1 in the hole 5 of opening in the state of non-contact, the path of the hole 5 of opening may be made larger than the overall diameter of a burner tile 1, and a burner tile 1 may be inserted in the hole 5 of opening. Since a clearance is generated between the hole 5 of opening, and a burner tile 1 in these cases, the heat in a furnace is made not to escape this clearance out of a furnace using sealants, such as mortar or a blanket. And after once removing a sealant and fixing an include angle, it is made for a sealant to close a clearance again, when changing the include angle of a burner tile 1.
[0029] The example of adjustable structure can be used also for the burner 2 of a melting basin whenever [ flame radiation angle / which was shown with the gestalten 1 and 2 of the above operation ]. When it uses for the burner 2 of a melting basin, effectiveness as taken below is done so.
[0030] 1. When the batch crest of the raw materials for glass which are floating in a melting basin has reached to near the front wall of a melting basin, or when it has floated near a detached building front wall from the batch crest of raw materials for glass with non-melting, the flame of a burner can be emitted aiming at the tip of a batch crest, or a suspension non-melting raw material. So, the poor glass from which the tip of a batch crest is pulled back to a doghouse side, or it becomes possible from which to fuse completely the non-melting raw material which separates from a batch crest and is floating in a melting basin, and a non-melting raw material becomes a cause at glass mold goods can be reduced.

[0031] 2. When the location at the tip of a batch crest gets mixed up by change of the input of raw materials for glass etc. in the case of the glass melting furnace to which the flame of the tip ****** burner 2 of a batch crest is emitted from the side attachment wall by the side of a front wall from the point of the batch crest of the raw materials for glass which are floating in a melting basin, whenever [ flame radiation angle / of a burner 2 ] can be changed, and it can follow in footsteps at the tip of a batch crest.
[0032] 3. When the hot spots in the melting basin at the time of a glass melting furnace design differ rather than the location which was being planned at the beginning, the location which changes whenever [ flame radiation angle / of a burner 2 ], corrects the hot spot in a melting basin, and is considered as a request can be made to produce a hot spot.
[0033] (Gestalt 3 of operation) the gestalt 3 of this operation is the burner 2 used for the furnace wall of the melting basin of a glass melting furnace, whenever [ flame radiation angle / of the gestalt 1 of the above-mentioned implementation ], in adjustable structure, is an example when using at which secondary air is used, and is notionally shown in drawing 3 . The gestalt 3 of this operation connects the burner casing 8 to the back end of a burner tile 1 in the flame radiation angle degree adjustable structure shown with the gestalt 1 of the above-mentioned implementation.
[0034] This burner casing 8 has the burner-tile end connection 9 connected with a burner tile 1, the burner insertion opening 10 with which a burner 2 is inserted, and the secondary air induction inlet 11 which introduces secondary air.
[0035] When leaning whenever [ flame radiation angle / of the burner 2 using this burner casing 8 ] in the direction of arbitration, a burner tile 1, the burner casing 8, and a burner 2 move together. At the time of this tilt actuation, the burner 2 is fixed to the burner casing 8 so that the pin center,large of the burner 2 inserted in the burner casing 8 may not shift.
[0036] Thus, since the heating value of the flame of a burner 2 other than the effectiveness explained above by adopting adjustable structure as the burner 2 using the secondary air used for the melting basin of a glass melting furnace whenever [ flame radiation angle / of this invention ] increases, adjustable structure is [ whenever / flame radiation angle / of this invention ] employable also as the furnace where the melting capacity of a glass melting furnace is big.
[0037] In addition, with the gestalt 3 of this operation, although the flame radiation angle degree adjustable structure of the gestalt 1 of operation was used, the flame radiation angle degree adjustable structure of the gestalt 2 of operation may be used.

---

[Translation done.]

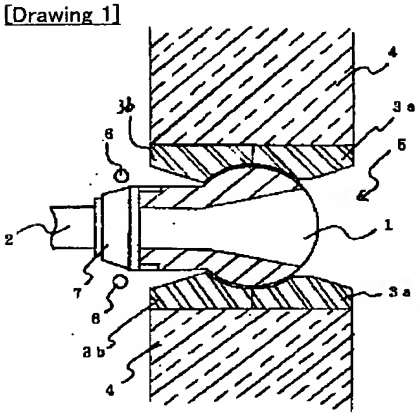
## DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the sectional view having shown the gestalt of 1 operation of this invention.
[Drawing 2] It is the sectional view having shown the gestalt of other operations of this invention.
[Drawing 3] It is the sectional view having shown the gestalt of other operations of this invention.
[Drawing 4] It is the sectional view of the conventional founding tub.
[Description of Notations]
1 — Burner tile 2 — Burner 3 — Burner block 3a — Inner block
3b — Outer block 4 — Furnace wall 5 — Hole of opening 6 — Ayr pipe 7 — Hardware
8 — Burner casing

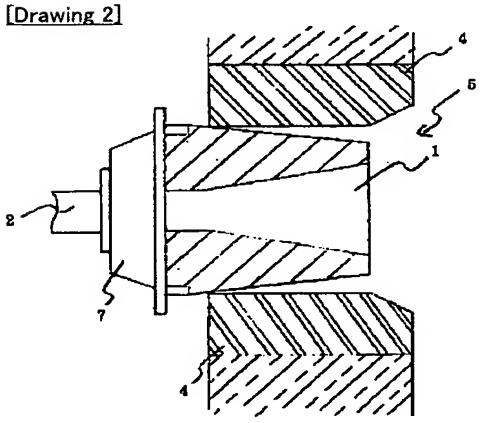
[Translation done.]

## DRAWINGS

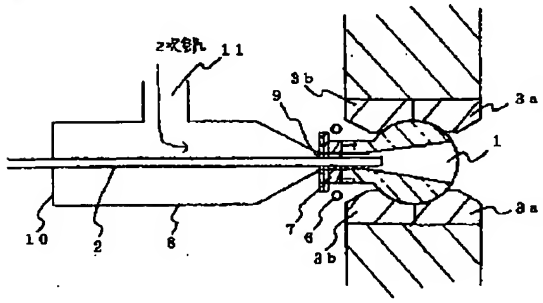
[Drawing 1]



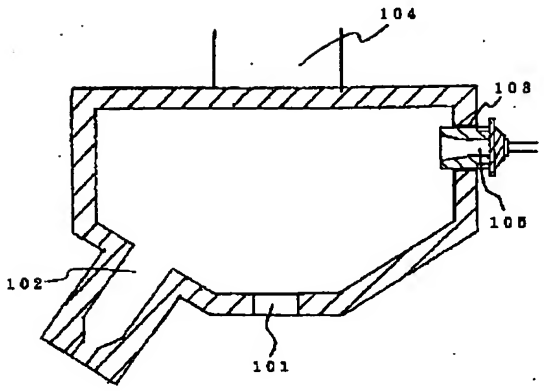

[Drawing 2]




[Drawing 3]




[Drawing 4]




[Translation done.]

(19)日本国特許庁（ＪＰ）　(12)公開特許公報（Ａ）　(11)特許出願公開番号

特開平９－２６３０４９

(43)公開日　平成９年（１９９７）１０月７日

| (51)Int.Cl.[6] | 識別記号 | 庁内整理番号 | ＦＩ | | 技術表示箇所 |
|---|---|---|---|---|---|
| B41M 5/26 | | | B41M 5/18 | 101 C | |
| | | | | B | |
| | | | | 101 E | |
| | | | | 111 | |

審査請求　未請求　請求項の数６　ＯＬ　（全８頁）

(21)出願番号　特願平８－７２２２６

(22)出願日　平成８年（１９９６）３月２７日

(71)出願人　０００００６７４７
株式会社リコー
東京都大田区中馬込１丁目３番６号
(72)発明者　森　泰智
東京都大田区中馬込１丁目３番６号　株式会社リコー内
(72)発明者　森田　充展
東京都大田区中馬込１丁目３番６号　株式会社リコー内
(72)発明者　成瀬　充
東京都大田区中馬込１丁目３番６号　株式会社リコー内
(74)代理人　弁理士　小松　秀岳　（外３名）

最終頁に続く

(54)【発明の名称】感熱記録材料

(57)【要約】
【課題】　耐水性、耐熱性、耐可塑剤性及びヘッドマッチング性（カス付着）に優れた感熱記録材料を提供する。
【解決手段】　支持体上に熱により呈色する感熱記録層を設け、更に該感熱記録層上に樹脂及び架橋剤を含有する保護層を設けた感熱記録材料において、該樹脂がアクリル系重合体又は共重合体のシードエマルジョンの存在下で、アクリルアミド及び／又はメタクリルアミドを重合して得られるコアシェル型エマルジョンであり、及び該架橋剤としてカルボジイミド化合物であることを特徴とする感熱記録材料。

1

【特許請求の範囲】

【請求項１】　支持体上に熱により呈色する感熱記録層を設け、更に該感熱記録層上に樹脂及び架橋剤を含有する保護層を設けた感熱記録材料において、該樹脂がアクリル系重合体又は共重合体のシードエマルジョンの存在下で、アクリルアミド及び／又はメタクリルアミドを重合して得られるコアシェル型エマルジョンであり、及び該架橋剤がカルボジイミド化合物であることを特徴とする感熱記録材料。

【請求項２】　該樹脂のコア部のガラス転移点Ｔｇが１５℃以上であることを特徴とする請求項１記載の感熱記録材料。

【請求項３】　該樹脂のシェル部のガラス転移点Ｔｇが１５０℃以上であることを特徴とする請求項１記載の感熱記録材料。

【請求項４】　該樹脂のコア部のガラス転移点Ｔｇが１５℃以上、かつシェル部のガラス転移点Ｔｇが１５０℃以上であることを特徴とする請求項１記載の感熱記録材料。

【請求項５】　更に顔料を併用し、顔料／樹脂比率が１以下であることを特徴とする請求項１ないし４記載の感熱記録材料。

【請求項６】　該顔料の吸油量が２５０ｃｃ／１００ｇ以下、かつその平均粒子径が３μｍ以下であることを特徴とする請求項５記載の感熱記録材料。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は感熱記録材料に関し、更に詳しくは熱により呈色する感熱記録層を支持体上に設けた感熱記録材料の改良に関する。

【０００２】

【従来の技術】一般に紙、フィルム等の支持体上に、熱発色性組成物を主成分とした感熱発色層を設けた感熱記録材料は、熱ヘッド・熱ペン・レーザー光・ストロボランプ等で加熱することで発色画像が得られる。この種の記録材料は、他の記録材料に比べ、記録時に煩雑な操作、装置が不要であり、短時間で記録でき、騒音の発生及び環境汚染が少ないこと、コストが安いことなどの利点のため、図書、文書などの複写に用いられる他、ファクシミリ、電子計算機、レコーダー、ラベル、券売機等多方面な記録材料として用いられている。このような感熱記録材料に用いられる熱発色性組成物は一般に発色剤と、この発色剤を熱時発色せしめる顕色剤とからなり、発色剤としては例えばラクトン、ラクタム又はスピロピラン環を有する無色又は淡色のロイコ染料が、また顕色剤としては従来から有機酸、フェノール性物質が用いられている。この発色剤と顕色剤とを組合せた記録材料は、殊に得られる画像の色調が鮮明であり、かつ地肌の白色度が高く、しかも画像の耐候性が優れているという利点を有し、広く利用されている。

2

【０００３】しかしながら、この種の感熱記録材料は水やＤＯＡ、ＤＯＰ等の可塑剤に接触すると画像が消失したり、油、エタノール、酢酸エチル等の溶剤により白色部が発色したり、画像信頼性に劣るという欠点が存在する。これらの改善として、感熱記録層上に保護層を設けることが提案されている（特開昭５４－１２８３４７号、特開昭５４－３５９４号）。このような保護層には、耐油性、耐可塑剤性を高める為に水溶性樹脂、例えばポリビニルアルコールとその変性タイプ、澱粉とその変性タイプ等が有効であるという提案もなされており（特開昭５６－１２６１９３号、特開昭５６－１３９９３号）、水溶性樹脂が主に用いられている。又、共重合体エマルジョンを保護層として用いることを提案されている（特開平５－６９６６５号）。しかしこのような水溶性樹脂を用いた保護層には耐水性が欠ける場合が多く、架橋剤を併用することで保護層を硬化させる方法（特開昭５７－１８８３９２号）がよく用いられている。架橋剤としては多くのものが提案されているが、それぞれ不充分な問題が残されている。例えばグリシジル系架橋剤（特開昭５７－１８８３９２号）を用いることで耐油性、耐マッチング性（熱ヘッドのカズ付着）に優れたものが提案されているが、反応性が良くなく耐水性としては充分といえない。

【０００４】アミノ化合物にグリオキシジル系架橋剤を使用した保護層（特開昭６４－６１２８７号）は耐水性、耐薬品性に優れるが、ホルマリンを発生するので食品用ラベルの使用には不適である。さらにアミノ基を含む架橋剤に関しては、保護層の異変を引き起こし、アジリジン系架橋剤は水溶液中で不安定であり、グリシジルアミン系架橋剤に関してはホルマリン発生等の問題が残されている。エポキシ系架橋剤の使用（特開昭４９－３６３４３号、特開昭６０－６８９９０号、特開平５－３１８９２６号）が提案されているが、芳香環を有する物は耐可塑剤性に劣り、グリコールタイプのものは耐熱性、地肌発色等の問題点を残している。又、これら方法は感度を低下させたり、サーマルヘッドとのマッチング性（カス付着性、印字かすれ等）の欠点を有している。

【０００５】

【発明が解決しようとする課題】本発明は前記の問題点を克服し、耐可塑剤性、耐熱性及び耐水性に優れ、発色濃度が高く、又記録部の消色や非印字部の発色防止にも優れ、さらにサーマルヘッドとの、マッチング性、ステッキング等にも優れた感熱記録材料を提供することを目的とする。

【０００６】

【課題を解決するための手段】本発明者らは鋭意検討した結果、樹脂及び架橋剤を含有する保護層を設けた感熱記録材料において、特定の樹脂と架橋剤の組み合せて用いることにより上記課題が解決されることを見出し本発明に至った。即ち、本発明は以下の（１）～（６）であ

る。

【０００７】（１）支持体上に熱により呈色する感熱記録層を設け、更に該感熱記録層上に樹脂及び架橋剤を含有する保護層を設けた感熱記録材料において、該樹脂がアクリル系重合体又は共重合体のシードエマルジョンの存在下で、アクリルアミド及び／又はメタクリルアミドを重合して得られるコアシェル型エマルジョンであり、及び該架橋剤がカルボジイミド化合物であることを特徴とする感熱記録材料。

（２）該樹脂のコア部のガラス転移点Ｔｇが１５℃以上であることを特徴とする前記（１）記載の感熱記録材料。

（３）該樹脂のシェル部のガラス転移点Ｔｇが１５０℃以上であることを特徴とする前記（１）記載の感熱記録材料。

【０００８】（４）該樹脂のコア部のガラス転移点Ｔｇが１５℃以上、かつシェル部のガラス転移点Ｔｇが１５０℃以上であることを特徴とする前記（１）記載の感熱記録材料。

（５）更に顔料を併用し、顔料／樹脂比率が１以下であることを特徴とする前記（１）ないし（４）記載の感熱記録材料。

（６）該顔料の吸油量が２５０ｃｃ／１００ｇ以下、かつその平均粒子径が３μｍ以下であることを特徴とする前記（５）記載の感熱記録材料。

【０００９】本発明の感熱記録材料の保護層に用いる樹脂は、アクリル系重合体又は共重合体のシードエマルジョンの存在下で、アクリルアミド及び／又はメタクリルアミドを重合して得られるコアシェル型エマルジョンの共重合体樹脂である。該共重合体樹脂は機能分離型であるため、バリア性、ヘッドマッチング性に関して好ましい作用効果を与える。該共重合体樹脂は従来の方法で製造することができる。また該樹脂のコア部においては、アクリロニトリルを用いることが好ましく、更にはＴｇを１５℃以上にすると良い。更に該樹脂のシェル部においてはアクリルアミド又は／及びメタクリルアミドの少なくとも１種を用い、Ｔｇを１５０℃以上になるようにその他のビニル単量体を選定するのが好ましい。このように、これらの保護層に用いる共重合体樹脂は、それらを製造するに当たって、必要に応じて他の共重合性単量体を併用して共重合させてもよい。

【００１０】本発明の保護層に用いる樹脂は前記したものであるが、これらと従来から保護層に用いられている樹脂を併用することも可能である。併用可能な樹脂としては、一般に公知である天然樹脂（例えば、アルギン酸ソーダ、澱粉、カゼイン、セルロース）や合成樹脂が任意に使用できるが、中でもポリビニルアルコール、ポリカルボン酸化合物、ポリアクリルアミド及びこれらの変性物又は誘導体であるものがアジリジンとの反応性及び成膜性によい。変性物又は誘導体とは、ポリビニルアルコール、ポリカルボン酸化合物、ポリアクリルアミドを含有し、その他の成分を共重合やグラフト重合させるか、もしくは官能基にペンダントとして結合させた化合物を意味する。更にポリビニルアルコール（ＰＶＡ）の中でも、エポキシ基変性ＰＶＡ、シラノール基変性ＰＶＡ、アセトアセチル基変性ＰＶＡ、アクリルアミド変性ＰＶＡ、ブチラール化ＰＶＡ－マレイン酸共重合体、Ｎ－メチロールウレタン化ＰＶＡ、アミノ基変性ＰＶＡ及び完全ケン化ＰＶＡが良好な結果を示す。完全ケン化ＰＶＡはケン化度８０％以上の物が好ましい。特に良好なものは、エポキシ基変性ＰＶＡである。又、ポリカルボン酸化合物の中では、スチレン－アクリル酸共重合体、アクリル酸エステル－アクリル酸共重合体、スチレン－アクリル酸エステル－アクリル酸共重合体、スチレン－マレイン酸共重合体、イソブチレン－無水マレイン酸共重合体及びこの誘導体、スチレン－アクリル酸－アクリルアミド共重合体が好ましい。特に好ましいものは、イソブチレン－無水マレイン酸共重合体及びこの誘導体かスチレン－アクリルアミド共重合体である。更にポリエチレンイミン、水性ポリエステル、水性ポリウレタン、ポリエステル、ポリウレタン、アクリル酸エステル系（共）重合体、エポキシ樹脂、ポリ酢酸ビニル、ポリ塩化ビニリデン、ポリ塩化ビニル及びこれらの誘導体等の水性エマルジョン樹脂等が挙げられる。

【００１１】本発明の感熱記録材料において、樹脂に更に架橋剤を組み合わせた保護層を設けることにより、耐水性、耐可塑剤性、耐熱性が優れたものとなる。又、本発明において架橋剤として用いるられるカルボジイミド化合物の具体例としては、下記のものが挙げられる。

$$R-N=C=N-R'$$

（式中、Ｒ：Ｒ'は置換されてもよいアルキル基又はアリール基）このような市販品としてはグンゼ産業、ＵＣＡＲＬＮＫ　ＸＬ２５ＳＥやグンゼ産業、ＵＣＡＲＬＮＫ　ＸＬ２７ＨＳ等が挙げられる。

【００１２】本発明において任意成分として用いられる顔料は従来公知のものが使用できる。例えば、二酸化ケイ素、ケイ酸カルシウム、ケイ酸マグネシウム、ケイ酸アルミニウム、ケイ酸亜鉛、酸化亜鉛、炭酸カルシウム、硫酸バリウム、酸化チタン、リトポン、タルク、ロウ石、カオリン、水酸化アルミニウム、焼成カオリンなどの無機顔料、尿素ホルマリン樹脂、ポリエチレン粉末等の有機顔料などが挙げられる。

【００１３】顔料と樹脂の比率は１以下である。又、顔料は吸油量が２５０ｃｃ／１００ｇ以下及び平均粒径が３μｍ以下であることが好ましい。本発明の保護層においては、前記の樹脂、架橋剤、顔料の他に、必要に応じ、この種の感熱記録材料に慣用される補助添加成分、例えば界面活性剤、紫外線吸収剤、熱可融性物質（又は滑剤）、圧力発色防止剤等を併用することができる。本発明において用いる熱により呈色させる方式としては、

5

ロイコ染料と顕色剤との発色反応を利用するもの、ジアゾ化合物とカップラーの反応を利用するもの、イソシアナートとアミンの反応を利用するものなどがある。本発明の特徴は感熱記録材料の保護層にあるので、特に発色方式を限定するものではない。以下、感熱記録方式として、一般的なロイコ染料を用いた方式のものについて説明を進める。

【００１４】本発明の感熱記録層において用いるロイコ染料は単独又は２種以上混合して適用されるが、このようなロイコ染料としては、この種の感熱材料に適用されているものが任意に適用され、例えば、トリフェニルメタン系、フルオラン系、フエノチアジン系、オーラミン系、スピロピラン系、インドリノフタリド系等の染料のロイコ化合物が好ましく用いられる。このようなロイコ染料の具体例としては、例えば、以下に示すようなものが挙げられる。

【００１５】即ち、３，３－ビス（ｐ－ジメチルアミノフェニル）－フタリド、３，３－ビス（ｐ－ジメチルアミノフェニル）－６－ジメチルアミノフタリド（別名クリスタルバイオレットラクトン）、３，３－ビス（ｐ－ジメチルアミノフェニル）－６－ジエチルアミノフタリド、３，３－ビス（ｐ－ジメチルアミノフェニル）－６－クロルフタリド、３，３－ビス（ｐ－ジブチルアミノフェニル）フタリド、３－シクロヘキシルアミノ－６－クロルフルオラン、３－ジメチルアミノ－５，７－ジメチルフルオラン、３－ジエチルアミノ－７－クロロフルオラン、３－ジエチルアミノ－７－メチルフルオラン、３－ジエチルアミノ－７，８－ベンズフルオラン、３－ジエチルアミノ－６－メチル－７－クロルフルオラン、３－（Ｎ－ｐ－トリル－Ｎ－エチルアミノ）－６－メチル－７－アニリノフルオラン、３－ピロリジノ－６－メチル－７－アニリノフルオラン、２－〔Ｎ－（３’－トリフルオルメチルフェニル）アミノ〕－６－ジエチルアミノフルオラン、２－〔３，６－ビス（ジエチルアミノ）－９－（ｏ－クロルアニリノ）キサンチル安息香酸ラクタム〕、３－ジエチルアミノ－６－メチル－７－（ｍ－トリクロロメチルアニリノ）フルオラン、３－ジエチルアミノ－７－（ｏ－クロルアニリノ）フルオラン、３－ジ－ｎ－ブチルアミノ－７－（ｏ－クロルアニリノ）フルオラン、３－Ｎ－メチル－Ｎ，ｎ－アミルアミノ－６－メチル－７－アニリノフルオラン、３－Ｎ－メチル－Ｎ－シクロヘキシルアミノ－６－メチル－７－アニリノフルオラン、３－ジエチルアミノ－６－メチル－７－アニリノフルオラン、３－（Ｎ，Ｎ－ジエチルアミノ）－５－メチル－７－（Ｎ，Ｎ－ジベンジルアミノ）フルオラン、ベンゾイルロイコメチレンブルー、６’－クロロ－８’－メトキシ－ベンゾインドリノースピロピラン、６’－ブロモ－３’－メトキシ－ベンゾインドリノースピロピラン、３－（２’－ヒドロキシ－４’－ジメチルアミノフェニル）－３－（２’－メトキシ－５’－クロルフェニル）フタリド、３－（２’－ヒドロキシ－４’－ジメチルアミノフェニル）－３－（２’メトキシ－５’－ニトロフェニル）フタリド、３－（２’－ヒドロキシ－４’－ジエチルアミノフェニル）－３－（２’－メトキシ－５’－メチルフェニル）フタリド、３－（２’－メトキシ－４’－ジメチルアミノフェニル）－３－（２’－ヒドロキシ－４’－クロル－５’－メチルフェニル）フタリド、３－（Ｎ－エチル－Ｎ－テトラヒドロフルフリル）アミノ－６－メチル－７－アニリノフルオラン、３－Ｎ－エチル－Ｎ－（２－エトキシプロピル）アミノ－６－メチル－７－アニリノフルオラン、３－Ｎ－メチル－Ｎ－イソブチル－６－メチル－７－アニリノフルオラン、３－モルホリノ－７－（Ｎ－プロピル－トリフルオロメチルアニリノ）フルオラン、３－ピロリジノ－７－ｍ－トリフルオロメチルアニリノフルオラン、３－ジエチルアミノ－５－クロロ－７－（Ｎ－ベンジル－トリフルオロメチルアニリノ）フルオラン、３－ピロリジノ－７－（ジ－ｐ－クロルフェニル）メチルアミノフルオラン、３－ジエチルアミノ－５－クロル－７－（α－フェニルエチルアミノ）フルオラン、３－（Ｎ－エチル－ｐ－トルイジノ）－７－（α－フェニルエチルアミノ）フルオラン、３－ジエチルアミノ－７－（ｏ－メトキシカルボニルフェニルアミノ）フルオラン、３－ジエチルアミノ－５－メチル－７－（α－フェニルエチルアミノ）フルオラン、３－ジエチルアミノ－７－ピペリジノフルオラン、２－クロロ－３－（Ｎ－メチルトルイジノ）－７－（ｐ－ｎ－ブチルアニリノ）フルオラン、３－（Ｎ－メチル－Ｎ－イソプロピルアミノ）－６－メチル－７－アニリノフルオラン、３－ジ－ｎ－ブチルアミノ－６－メチル－７－アニリノフルオラン、３，６－ビス（ジメチルアミノ）フルオレンスピロ（９，３’）－６’－ジメチルアミノフタリド、３－（Ｎ－ベンジル－Ｎ－シクロヘキシルアミノ）－５，６－ベンゾ－７－α－ナフチルアミノ－４’－ブロモフルオラン、３－ジエチルアミノ－６－クロル－７－アニリノフルオラン、３－ジエチルアミノ－６－メチル－７－メシチジノ－４’，５’－ベンゾフルオラン、３－Ｎ－メチル－Ｎ－イソプロピル－６－メチル－７－アニリノフルオラン、３－Ｎ－エチル－Ｎ－イソアミル－６－メチル－７－アニリノフルオラン、３－ジエチルアミノ－６－メチル－７－（２’，４’－ジメチルアニリノ）フルオラン、３－モルホリノ－７－（Ｎ－プロピル－トリフルオロメチルアニリノ）フルオラン、３－ピロリジノ－７－トリフルオロメチルアニリノフルオラン、３－ジエチルアミノ－５－クロロ－７－（Ｎ－ベンジル－トリフルオロメチルアニリノ）フルオラン、３－ピロリジノ－７－（ジ－Ｐ－クロルフェニル）メチルアミノフルオラン、３－ジエチルアミノ－５－クロル－７－（α－フェニルエチルアミノ）フルオラン、３－（Ｎ－エチル－Ｐ－トルイジノ）－７－（α－フェニルエチ

6

ルアミノ）フルオラン、３－ジエチルアミノ－７－（ｏ－メトキシカルボニルフェニルアミノ）フルオラン、３－ジエチルアミノ－５－メチル－７－（α－フェニルエチルアミノ）フルオラン、３－ジエチルアミノ－７－ピペリジノフルオラン、２－クロロ－３－（Ｎ－メチルトルイジノ）－７－（ｐ－Ｎ－ブチルアニリノ）フルオラン、３，６－ビス（ジメチルアミノ）フルオレンスピロ（９，３’）－６’－ジメチルアミノフタリド、３－（Ｎ－ベンジル－Ｎ－シクロヘキシルアミノ）－５，６－ベンゾ－７－α－ナフチルアミノ－４’－ブロモフルオラン、３－ジエチルアミノ－６－クロル－７－アニリノフルオラン、３－Ｎ－エチル－Ｎ－（－２－エトキシプロピル）アミノ－６－メチル－７－アニリノフルオラン、３－Ｎ－エチル－Ｎ－テトラヒドロフルフリルアミノ－６－メチル－７－アニリノフルオラン、３－ジエチルアミノ－６－メチル－７－メシチジノ－４’，５’－ベンゾフルオラン、３－（ｐ－ジメチルアミノフェニル）－３－｛１，１－ビス（ｐ－ジメチルアミノフェニル）エチレン－２－イル｝フタリド、３－（ｐ－ジメチルアミノフェニル）－３－｛１，１－ビス（Ｐ－ジメチルアミノフェニル）エチレン－２－イル｝－６－ジメチルアミノフタリド、３－（ｐ－ジメチルアミノフェニル）－３－（１－ｐ－ジメチルアミノフェニル－１－フェニルエチレン－２－イル）フタリド、３－（ｐ－ジメチルアミノフェニル）－３－（１－ｐ－ジメチルアミノフェニル－１－ｐ－クロロフェニルエチレン－２－イル）－６－ジメチルアミノフタリド、３－（４’－ジメチルアミノ－２’－メトキシ）－３－（１”－ｐ－ジメチルアミノフェニル－１”－ｐ－クロロフェニル－１”，３”－ブタジエン－４”－イル）ベンゾフタリド、３－（４’－ジメチルアミノ－２’－ベンジルオキシ）－３－（１”－ｐ－ジメチルアミノフェニル－１”－フェニル－１”，３”－ブタジエン－４”－イル）ベンゾフタリド３－ジメチルアミノ－６－ジメチルアミノ－フルオレン－９－スピロ－３’－（６’－ジメチルアミノ）フタリド、３，３－ビス｛２－（ｐ－ジメチルアミノフェニル）－２－（ｐ－メトキシフェニル）エテニル｝－４，５，６，７－テトラクロロフタリド、３－ビス｛１，１－ビス（４－ピロリジノフェニル）エチレン－２－イル｝－５，６－ジクロロ－４，７－ジブロモフタリド、ビス（ｐ－ジメチルアミノスチリル）－１－ナフタレンスルホニルメタン、ビス（ｐ－ジメチルアミノスチリル）－１－ｐ－トリルスルホニルメタン等。

【００１６】また本技術において、顕色剤としては、前記ロイコ染料を接触時発色させる電子受容性の化合物、例えばフェノール性化合物、チオフェノール性化合物、チオ尿素誘導体、有機酸及びその金属塩等を使用することができ、その具体例としては以下に示すものがあげられるが、これに限られるわけではない。

【００１７】４，４’－イソプロピリデンジフェニール、４，４’－イソプロピリデンビス（ｏ－メチルフェノール）、４，４’－セカンダリーブチリデンビスデノール４，４’－イソプロピリデンビス（２－ターシャリーブチルフェノール）、ｐ－ニトロ安息香酸亜鉛、１，３，５－トリス（４－ターシャリーブチル－３－ヒドロキシ－２，６－ジメチルベンジル）イソシアヌル酸、２，２－（３，４’－ジヒドロキシジフェニル）プロパン、ビス（４－ヒドロキシ－３－メチルフェニル）スルフィド、４－｛β－（ｐ－メトキシフェノキシ）エトキシ｝サリチル酸、１，７－ビス（４－ヒドロキシフェニルチオ）－３，５－ジオキサヘプタン、１，５－ビス（４－ヒドロキシフェニルチオ）－５－オキサペンタン、フタル酸モノベンジルエステルモノカルシウム酸、４，４’－シクロヘキシリデンジフェノール、４，４’－イソプロピリデンビス（２－クロロフェノール）、２，２’－メチレンビス（４－メチル－６－ターシャリーブチルフェノール）、４，４’－ブチリデンビス（６－ターシャリーブチル－２－メチル）フェノール、１，１，３－トリス（２－メチル－４－ヒドロキシ－５－ターシャリーブチルフェニル）ブタン、１，１，３－トリス（２－メチル－４－ヒドロキシ－５－シクロヘキシルフェニル）ブタン、４，４’－チオビス（６－ターシャリーブチル－２－メチル）フェノール、４，４’－ジフェノールスルホン、４－イソプロポキシ－４’－ヒドロキシジフェニルスルホン、４－ベンジロキシ－４’－ヒドロキシジフェニルスルホン、４，４’－ジフェノールスルホキシド、Ｐ－ヒドロキシ安息香酸イソプロピル、Ｐ－ヒドロキシ安息香酸ベンジル、プロトカテキユ酸ベンジル、没食子酸ステアリル、没食子酸ラウリル、没食子酸オクチル、１，３－ビス（４－ヒドロキシフェニルチオ）－プロパン、Ｎ，Ｎ’－ジフェニルチオ尿素、Ｎ，Ｎ’－ジ（ｍ－クロロフェニル）チオ尿素、サリチルアニリド、ビス－（４－ヒドロキシフェニル）酢酸メチル、ビス－（４－ヒドロキシフェニル）酢酸ベンジル、１，３－ビス（４－ヒドロキシクミル）ベンゼン、１，４－ビス（４－ヒドロキシクミル）ベンゼン、２，４’－ジフェノールスルホン、２，２’－ジアリル－４，４’－ジフェノールスルホン、３，４－ジヒドロキシフェニル－４’－メチルジフェニルスルホン、１－アセチルオキシ－２－ナフトエ酸亜鉛、２－アセチルオキシ－１－ナフトエ酸亜鉛、２－アセチルオキシ－３－ナフトエ酸亜鉛、α，α－ビス（４－ヒドロキシフェニル）－α－メチルトルエン、チオシアン酸亜鉛のアンチピリン錯体、テトラブロモビスフェノールＡ、テトラブロモビスフェノールＳ、４，４’－チオビス（２－メチルフェノール）、４，４’－チオビス（２－クロロフェノール）等が挙げられる。

【００１８】本技術の感熱記録材料を製造するために、ロイコ染料及び顕色剤を支持体上に結合させる場合、慣用の種々の結合剤を適宜用いることができ、その具体例

9

としては、例えば以下のものが挙げられる。

【００１９】即ち、ポリビニルアルコール、澱粉及びその誘導体、メトキシセルロース、ヒドロキシエチルセルロース、カルボキシメチルセルロース、メチルセルロース、エチルセルロース等のセルロース誘導体、ポリアクリル酸ソーダ、ポリビニルピロリドン、アクリルアミド／アクリル酸エステル共重合体、アクリルアミド／アクリル酸エステル／メタアクリル酸三元共重合体、スチレン／無水マレイン酸共重合体アルカリ塩、イソブチレン／無水マレイン酸共重合体アルカリ塩、ポリアクリルアミド、アルギン酸ソーダ、ゼラチン、カゼイン等の水溶性高分子の他、ポリ酢酸ビニル、ポリウレタン、ポリアクリル酸エステル、ポリメタクリル酸エステル、塩化ビニル／酢酸ビニル共重合体、エチレン／酢酸ビニル共重合体等のエマルジョンやスチレン／ブタジエン共重合体、スチレン／ブタジエン／アクリル系共重合体等のラテックス等。

【００２０】又、本発明の感熱記録層においては、前記ロイコ染料及び顕色剤と共に、必要に応じ、この種の感熱記録材料に慣用される補助添加成分、例えば、フィラー、界面活性剤、熱可融性物質（又は滑剤）、圧力発色防止剤等を併用することができる。この場合、フィラー及び熱可融性物質の具体例としては、前記保護層との関連で例示されたものと同様のものが挙げられる。

【００２１】本発明においては、支持体と感熱記録層の間にアンダーコート層を設けることも可能である。この場合、アンダーコート層を構成する主成分としては、前記保護層において用いた樹脂と架橋剤が好ましく使用さ

10

れる。このような構成にすると、支持体裏面から浸出する水や薬品に対する耐水性や耐薬品性が優れたものとなる。又、本発明においては、支持体の裏面にバックコート層を設けることができるが、この場合の主成分としても前記保護層において用いた樹脂と架橋剤を用いることが望ましい。かかる構成によれば、支持体裏面からの水や薬品の浸出を効果的に抑制することができる。更に、本発明においては、保護層を２層以上構成することも可能である。

【００２２】本発明の感熱記録材料は、種々の分野において利用されるが、殊に前記した優れた発色画像及び地肌部の安定性を利用し、感熱記録型ラベルシートや、感熱記録型磁気券紙として有利に利用することができる。感熱記録型ラベルシートの場合、支持体の一方の面に、前記したロイコ染料及び顕色剤を含有する感熱記録層と前記保護層を設け、支持体の他方の面に、接着剤層を介して剥離台紙を設ければよく、磁気券紙の場合は、この剥離台紙に代えて、強磁性体と結合剤とを主成分とする磁気記録層を設ければよい。

【００２３】

【発明の実施の形態】以下、本発明を実施例及び比較例を用いて詳細に説明する。なお、以下の部及び％はいずれも重量基準である。

実施例１～１１、比較例１～３

＜感熱記録層の形成＞下記組成からなる混合物をそれぞれサンドグライダーで２～４時間粉砕分散して、〔Ａ液〕及び〔Ｂ液〕を調整した。

【００２４】

〔Ａ液〕

| | |
|---|---|
| ３－（Ｎ－メチル－Ｎ－シクロヘキシル）アミノ－６－メチル－７－アニリノフルオラン | １０部 |
| ポリビニルアルコールの１０％水溶液 | １０部 |
| 水 | ８０部 |

〔Ｂ液〕

| | |
|---|---|
| ４－ヒドロキシフェニル－４’－イソプロポキシフェニルスルホン | １０部 |
| 炭酸カルシウム | １０部 |
| １，１，３－トリス（２－メチル－４－ヒドロキシ－５－シクロヘキシル）フェニルブタン | ５部 |
| ポリビニルアルコールの１０％水溶液 | ２０部 |
| 水 | |

更に〔Ａ液〕、〔Ｂ液〕ともにサンドミルにて２４時間分散し各分散液を得て、重量比が〔Ａ液〕：〔Ｂ液〕＝１：３となるよう混合撹拌して感熱記録層塗布液を調製し、市販上質紙に乾燥後塗布量が坪量５０ｇ／ｍ$^2$、乾燥重量が５ｇ／ｍ$^2$になるように塗布乾燥して感熱記録層塗布済紙を得た。

【００２５】＜保護層の形成＞表１に示される樹脂、架橋剤、顔料種及び顔料添加部を用い、下記組成からなる混合物を調整した。

| | |
|---|---|
| 樹脂２０％　水分散体又は水溶液 | １００部 |
| 架橋剤１０％　水分散体又は水溶液 | １０部 |
| 顔料２０％　分散液又は水 | Ｘ部 |

前記感熱記録層形成済み上質紙上の記録層上、上質紙裏面上あるいは上質紙と感熱記録層の間に乾燥重量が３ｇ

／m²になるように塗布乾燥して所定の層を形成し、実施例１～１１、比較例１～３を作製した。用いた樹脂はコア部がアクリルニトリルを含有するアクリル系ポリマーでありシェル部がメタクリルアシド及び／又はアクリルアミドを含有するアクリル系ポリマーである。

【００２６】

【表１】

| | 樹脂 | | 架橋剤 | 顔料（シリカ） | | |
|---|---|---|---|---|---|---|
| | コアTg | シェルTg | | 吸油量 | 粒径 | 添加部 |
| 実施例1 | 20 | 180 | ダンゼ化学UCARLNK XL 25SE | 200 | 2 | 50 |
| 〃 2 | 〃 | 〃 | 〃 | 100 | 2 | 50 |
| 〃 3 | 〃 | 〃 | 〃 | 300 | 2 | 50 |
| 〃 4 | 〃 | 〃 | 〃 | 200 | 1 | 50 |
| 〃 5 | 〃 | 〃 | 〃 | 200 | 4 | 50 |
| 〃 6 | 〃 | 〃 | 〃 | 200 | 2 | 10 |
| 〃 7 | 〃 | 〃 | 〃 | 200 | 2 | 100 |
| 〃 8 | 20 | 180 | 〃 | － | | |
| 〃 9 | 10 | 180 | 〃 | － | | |
| 〃 10 | 10 | 100 | 〃 | － | | |
| 〃 11 | 20 | 100 | 〃 | － | | |
| 比較例1 | 10 | 180 | アジリダン TAZM 相互薬工 | － | | |
| 〃 2 | PVA | | ダンゼ化学UCARLNK XL 25SE | － | | |
| 〃 3 | 20 | 180 | － | | | |

【００２７】実施例１～１１及び比較例１～３について以下に示す試験を実施し、結果を表２に示す。

＜発色特性＞松下（株）製印字装置にて、０．６Ｗ、１．２ｍｓｅｃにて印字し、マクベス濃度測定機ＲＤ－９１４にて濃度を測定した。

【００２８】＜耐水性＞４０℃、１６時間放置後、水中に１６時間浸け、指で摩擦して剥れ状態を評価した。

○…剥がれなく良好

△…わずかに剥がれが生じる

×…剥れが生じて不良

＜耐熱性＞マクベス濃度計で測定したサンプルを７０℃、１時間放置後、再びマクベス濃度計で測定し、放置前後で地肌部で発色があるかどうか調べる。尚、試験前の地肌濃度は０．０７であった。

＜耐可塑剤性＞上記の如く印字したサンプルに、市販のポリラップを接着し、４０℃にて２４時間放置した場合の濃度の残存率を測定した。

【００２９】＜カス付着＞サーマルプリンターにて３０ｋｍ印字し、その後のサーマルヘッド上のカス付着を観察した。

◎…付着なし、印字に問題がない

○…やや付着しているが、印字には問題がない

×…著しく付着しており、印字に問題がある

【００３０】

【表２】

13　　14

| | 発色性 | 耐水性 | 耐熱性 | 耐可塑剤性 | カス付着ヘッドマッチング |
|---|---|---|---|---|---|
| 実施例１ | １．３５ | ○ | ０．１１ | ７４ | ◎ |
| 〃　２ | １．３４ | ○ | ０．１２ | ７９ | ○ |
| 〃　３ | １．３６ | ○ | ０．１１ | ７０ | ◎ |
| 〃　４ | １．３５ | ○ | ０．１２ | ７３ | ◎ |
| 〃　５ | １．３０ | ○ | ０．１２ | ７４ | ○ |
| 〃　６ | １．３７ | ○ | ０．１２ | ７３ | ◎ |
| 〃　７ | １．３６ | ○ | ０．１１ | ７０ | ◎ |
| 〃　８ | １．３５ | ○ | ０．１１ | ７８ | ○ |
| 〃　９ | １．３０ | ○ | ０．１１ | ７９ | ○ |
| 〃　１０ | １．２９ | ○ | ０．１２ | ７７ | ○ |
| 〃　１１ | １．３１ | ○ | ０．１１ | ７８ | ○ |
| 比較例１ | １．３０ | △ | ０．１９ | ６５ | × |
| 〃　２ | １．３２ | × | ０．１２ | ７０ | × |
| 〃　３ | １．３５ | × | ０．１２ | ７２ | × |

【００３１】

【発明の効果】表２から明らかなように、本発明の感熱記録材料はアクリル系（共）重合体のシードエマルジョンの存在下でアクリルアミド及び／又はメタクリルアミドを重合して得られるコアシェル型エマルジョンの共重合体樹脂を用い、これに架橋剤としてカルボジイミド化合物を用いた保護層を設けたため、耐水性、耐熱性、耐可塑剤性が優れたものとなる。又、これに顔料として吸油量２５０ｃｃ／１００ｇ以下、更に平均粒子径が３μｍ以下であると、ヘッドマッチング性（カス付着）、耐可塑剤性、発色特性に優れるものとなる。

---

フロントページの続き

(72)発明者　梶河　毅
東京都大田区中馬込１丁目３番６号　株式会社リコー内